

WE CLAIM:

1. A method for the preparation of a cross-linked proton exchange membrane, comprising:
providing a sulfonated polymer having a degree of sulfonation higher than 0.6;
dissolving the sulfonated polymer in a polar casting solvent;
adding at least one polyol cross-linking agent to obtain a solution, the at least one polyol cross-linking agent being added in a ratio of polyol molecules per repeat unit of the sulfonated polymer higher than or equal to 1 to generate cross-linking;
casting the solution to obtain the membrane; and
curing the membrane.
2. A method as claimed in claim 1, wherein the degree of sulfonation of the sulfonated polymer is higher than 0.75.
3. A method as claimed in any one of claims 1 and 2, wherein the ratio of polyol molecules per repeat unit of the sulfonated polymer is between 2 and 3.
4. A method as claimed in any one of claims 1 to 3, wherein the sulfonated polymer is dissolved in the polar casting solvent to a concentration ranging between 5 and 25 wt%.
5. A method as claimed in any one of claims 1 to 3, comprising wherein the sulfonated polymer is dissolved in the polar casting solvent to a concentration ranging between 10 and 15 wt%.
6. A method as claimed in any one of claims 1 to 5, comprising agitating the solution prior to casting.

7. A method as claimed in any one of claims 1 to 6, comprising outgassing the cast solution.
8. A method as claimed in any one of claims 1 to 7, comprising drying the cast solution at room temperature.
9. A method as claimed in any one of claims 1 to 8, comprising curing the membrane under vacuum.
10. A method as claimed in any one of claims 1 to 9, wherein the membrane is cured at gradually increasing temperature.
11. A method as claimed in any one of claims 1 to 10, wherein the membrane is cured at a temperature ranging between 25 and 180° C.
12. A method as claimed in any one of claims 1 to 10, wherein the membrane is cured at a temperature ranging between 25 and 150° C.
13. A method as claimed in any one of claims 1 to 12, wherein the sulfonated polymer comprises a sulfonated poly(ether ether ketone).
14. A method as claimed in any one of claims 1 to 13, wherein the polar casting solvent is selected from the group consisting of DMAc, NMP, DMF, butyrolactone, water, a mixture of water and acetone, and a mixture of water and alcohol.
15. A method as claimed in any one of claims 1 to 13, wherein the polar casting solvent is selected from the group consisting of water, a mixture of water and acetone, and a mixture of water and alcohol.
16. A method as claimed in any one of claims 1 to 15, wherein the at least one polyol cross-linking agent comprises a diol.

17. A method as claimed in any one of claims 1 to 15, wherein the at least one polyol cross-linking agent is selected from the group consisting of ethylene glycol and glycerol.
18. A method as claimed in any one of claims 1 to 17, comprising drying the sulfonated polymer prior to adding the at least one cross-linking agent.
19. A fuel cell using a cross-linked proton exchange membrane prepared in accordance with any one of claims 1 to 18.
20. A proton exchange membrane suitable for fuel cells, comprising : a cross-linked sulfonated polymer provided from a solution which has been cast and cured, the solution including a sulfonated polymer, having a degree of sulfonation higher than 0.6, dissolved in a polar casting solvent and at least one polyol cross-linking agent added to the dissolved sulfonated polymer in a ratio of the cross-linking agent molecules per repeat unit of the sulfonated polymer higher than or equal to 1 to generate cross-linking.
21. A proton exchange membrane as claimed in claim 20, wherein the sulfonated polymer has a degree of sulfonation higher than 0.75.
22. A proton exchange membrane as claimed in one of claims 20 and 21, wherein the ratio of polyol molecules per repeat unit of the sulfonated polymer in the solution is between 2 and 3.
23. A proton exchange membrane as claimed in any one of claims 20 to 22, wherein the sulfonated polymer is dissolved in the polar casting solvent to a concentration ranging between 5 and 25 wt%.
24. A proton exchange membrane as claimed in any one of claims 20 to 22, wherein the sulfonated polymer is dissolved in the polar casting solvent to a concentration ranging between 10 and 15 wt%.

25. A proton exchange membrane as claimed in any one of claims 20 to 24, wherein the cast solution is outgassed.
26. A proton exchange membrane as claimed in any one of claims 20 to 25, wherein the cast solution is dried at room temperature.
27. A proton exchange membrane as claimed in any one of claims 20 to 26, wherein the solution is cured under vacuum.
28. A proton exchange membrane as claimed in any one of claims 20 to 27, wherein the curing of the solution is carried out at a temperature that is gradually increased.
29. A proton exchange membrane as claimed in any one of claims 20 to 28, wherein the curing temperature ranges between 25 and 180° C.
30. A proton exchange membrane as claimed in any one of claims 20 to 28, wherein the curing temperature ranges between 25 and 150° C.
31. A proton exchange membrane as claimed in any one of claims 20 to 30, wherein the sulfonated polymer comprises sulfonated poly(ether ether ketone).
32. A proton exchange membrane as claimed in any one of claims 20 to 31, wherein the polar casting solvent is selected from the group consisting of DMAc, NMP, DMF, butyrolactone, water, a mixture of water and acetone, and a mixture of water and alcohol.
33. A proton exchange membrane as claimed in any one of claims 20 to 31, wherein the polar casting solvent is selected from the group consisting of water, a mixture of water and acetone, and a mixture of water and alcohol.

34. A proton exchange membrane as claimed in any one of claims 20 to 33, wherein the at least one polyol cross-linking agent comprises a diol.
35. A proton exchange membrane as claimed in any one of claims 20 to 33, wherein the cross-linking agent is selected from the group consisting of ethylene glycol and glycerol.
36. A proton exchange membrane as claimed in any one of claims 20 to 35, wherein the sulfonated polymer is dried prior to adding the at least one cross-linking agent.